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PRODUCTS OF THE HYPOCHLORITE OXIDATION OF HYDRAZINE FUELS

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Neutralization of hydrazine fuels with hypochlorite is a recommended procedure for the treatment of fuel spills prior to disposal. Previous research has shown that incomplete reaction of hypochlorite with the methylated hydrazine fuels monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) leads to a wide variety of byproducts, including N-nitrosoamines, which are believed to be highly carcinogenic. The results presented in this report were obtained as part of a program to assess the environmental implications of using the hypochlorite method for the treatment and disposal of hydrazine fuel spills. The fuels examined were hydrazine, MMH, UDMH, and Aerozine-50. The neutralization products were determined under experimental conditions comparable to those expected for actual spills. The effects of varying the temperature and the pH as well as of aging the final reaction mixture were determined. Quantitative measurements of the nitrosoamines produced are presented. Major and environmentally significant minor products were identified using gas chromatography/mass-spectrometry.

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PREFACE

This report was prepared by the Energy and Environmental Systems Division, Argonne National Laboratory (EES/ANL) under Inter-Agency Agreement No. N85-14 (MIPR) for the Air Force Engineering and Services Center, Engineering and Services Laboratory (AFESC/ESL), Tyndall Air Force Base, Florida 32403-6001. This work was sponsored by the U. S. Air Force Engineering and Services Center (AFESC). Surendra Joshi was the project officer. This report summarized work accomplished between 1 October 1984 and 31 September 1986.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

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INTRODUCTION

A. OBJECTIVE

The U.S. Air Force uses hydrazine (N_2H_4), monomethylhydrazine (MMH), 1,1-dimethylhydrazine (unsymmetrical dimethylhydrazine, or UDMH), and Aerozine-50 (AE-50, a 50-50 mixture by weight of hydrazine and UDMH) in a number of applications, including auxiliary power units, small thrusters, and space vehicles (Reference 1). The routine handling of these fuels occasionally results in the accidental spillage of small quantities, which must then be collected and disposed of by base personnel. Most hydrazine fuels are considered to be at least potentially carcinogenic, and a host of other toxic effects are known to result from exposure to these substances (References 1,2). The toxic nature of hydrazine fuels dictates that they must be treated and carefully disposed of in an environmentally acceptable manner in the event of accidental spills or contamination. This report describes studies related to one method for the disposal of these fuels. Specifically, the objective of the work described in this report was to identify and quantify major environmentally significant products of the chemical neutralization of these fuels with hypochlorite.

B. BACKGROUND

A possible approach to treatment and disposal is to chemically react the collected fuel with a suitable oxidizing agent before disposal. The chemical oxidation of hydrazine itself has been studied for well over 80 years (Reference 1 and references therein), and more recently the oxidation of the methylated hydrazines has also been studied experimentally in both the liquid (References 1,3-21) and the gas phase (References 22-24). If a chemical neutralization is to be carried out by base personnel, however, the oxidizing agent should be cheap, easy to obtain, and easy to use. Ordinary household or commercial chlorine bleach fulfills these requirements. Liquid household bleach is a solution of sodium hypochlorite (NaClO) in water, and a commonly available dry bleach is the HTH® brand bleach manufactured by the Olin Corporation. HTH® comes in granular form and contains calcium hypochlorite ($Ca(ClO)_2$) and inert ingredients.

The use of a hypochlorite bleach for the neutralization of hydrazine has been recommended by Stauffer and Eyl (Reference 25) and Marsh and Knox (Reference 26), and for hydrazine fuels in general by Hannum (Reference 2). The chemical oxidation of hydrazine itself is often quantitative (References 1 and references therein, 27), but studies of the oxidation of methylated hydrazine fuels cited above have shown that these reactions are rarely, if ever, quantitative and that a wide variety of partial oxidation products are

usually formed. Because oxidation of methylated hydrazines is often incomplete, there is some reason for concern regarding the use of chemical neutralization procedures before the disposal of these fuels. However, little quantitative or qualitative information exists regarding the nature and amounts of various oxidation products when the reaction is carried out under conditions that approach those encountered in the field.

Relatively few studies have been published in which hypochlorite was the oxidizing agent. Castegnaro et al. (Reference 3) have evaluated four oxidative methods for the chemical neutralization of hydrazine and several methylated hydrazines, including the use of both sodium and calcium hypochlorite. Mach and Baumgartner (Reference 15) have examined the products of the reaction between calcium hypochlorite and UDMH, and Bray and Cuy (Reference 28) have studied the hypochlorite-hydrazine reaction.

The oxidation of hydrazine by chlorine has been studied by Rianda and Easton (Reference 17), Browne and Shetterly (Reference 29), Kirk and Browne (Reference 30), and Bray and Cuy (Reference 28). Other than the work of Rianda and Easton (Reference 17), Rianda et al. (Reference 18), and Koch and Fochtman (Reference 31), no studies exist of the products of the chlorinolysis of methylated hydrazines.

C. SCOPE

The research described in this report was undertaken to determine the identity of the important by-products of the reaction between hypochlorite and the methylated hydrazine fuels listed above. The work was conducted in two phases. In the first phase, emphasis was placed on the qualitative identification of reaction products. An important finding in phase one was that N-nitrosoalkylamines (or alkylnitrosoamines) were produced under a variety of conditions. These substances are known carcinogens (Reference 32), and in Phase 2 of this work, the quantification of the nitrosoamines produced was emphasized. The results of these studies are reported and discussed in the following sections. Some of these results have also been reported elsewhere (References 33,34).

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SECTION II

DESCRIPTION OF EXPERIMENTS

A. MATERIALS

The hydrazine fuels N_2H_4, MMH, and UDMH used in this study were technical grade, manufactured by the Olin Corporation, and were used without further purification. Technical grade corresponds most nearly to the purity used in applications by the Air Force. Anhydrous hydrazine was used. After opening, the bottles were flushed thoroughly with nitrogen before further storage. No discoloration or other degradation was observed when the fuels were stored in this way. Smaller amounts of each fuel were stored under nitrogen in a hood in clear glass-stoppered bottles sealed with Parafilm®. During the second phase of the project, stock 2 percent solutions of each fuel were also prepared in high-pressure liquid chromatography (HPLC)-grade water, flushed with nitrogen and stored in volumetric flasks sealed with Parafilm®. Stock quantities of AE-50 were prepared by mixing equal weights of the two constituents, and solutions were prepared as with the other fuels.

The sodium hypochlorite solution used was ordinary household bleach, nominally 5.25 percent NaClO. This concentration was checked by iodometric titration (Reference 35) of an early sample and was found to be accurate. The liquid bleach was used thereafter without further calibration.

When solid bleach was required, Olin Corporation HTH® brand bleach was used. HTH® is nominally 65 percent calcium hypochlorite and 35 percent inert ingredients. No check was made on the hypochlorite content of the HTH® samples.

The water used in the preparation of solutions was HPLC-grade bottled water and was used without further purification. The dichloromethane used to extract the reaction products from the final aqueous reaction mixture was HPLC-grade solvent, also used without further purification. Authentic samples of N-nitrosodimethylamine (NDMA), N-nitrosomethylethylamine (NEMA), and N-nitrosodiethylamine (NDEA) were obtained from Sigma Chemical Co. in septum-capped vials and were used as received in the preparation of analytical standards.

B. APPARATUS

The apparatus consisted of a three-necked Pyrex® flask that served as a reaction vessel, a calibrated addition funnel with which known quantities of liquid could be added to the flask, a Pyrex® cold trap and a gas buret. During the first phase of the program, a 2-liter flask was used as a reaction vessel, but during the second phase, a 500-mL flask was used instead. The reasons for the change were: (1) the 2-liter flask had been damaged and could

not be used, (2) experience from phase one indicated that large sample volumes were not needed to obtain good product samples for subsequent analyses, and (3) the use of smaller quantities of fuel would keep the quantity of evolved gas within the capacity of the gas buret and obviate the need for separate experiments to determine the quantity of gas produced. The addition funnel was attached to the middle neck of the reaction vessel. The space above the liquid in the addition funnel was connected by a length of plastic tubing to another neck on the reaction vessel to allow the free addition of liquid while maintaining a closed system. During an experiment, the evolved gas was passed from the reaction vessel through the cold trap and then to the gas buret. In the second phase of the program, the cold trap was omitted. The reaction mixture was stirred using a magnetic stirrer and a Teflon®-coated stirring bar.

The gas buret was constructed out of a clear polycarbonate plastic tube having an internal diameter of 4 inches. One end was sealed by cementing a plastic disk over it, and the other end was left open to accommodate a two-holed rubber stopper through which the tube carrying the gas to be collected was inserted. A scale was made by attaching a strip of precision graph paper, lengthwise, to the side using clear, waterproof polyethylene tape, and the buret was calibrated by adding known volumes of water using a 50-mL graduated cylinder and noting the corresponding water level as indicated by the scale reading. The overall accuracy attained was sufficient to allow useful measurements of the quantity of gas evolved to be made. The capacity of the buret was approximately 2 liters.

Normally, the reaction vessel was not thermostatted, and the reactions were carried out at room temperature (23 ± 1°C). In several runs during the second phase of the program, the temperature was controlled at levels significantly different from room temperature. In these cases, the reaction vessel was immersed in either hot water that was maintained at 45 ± 1°C by a continual flow of hot tap water, or in a salt water-ice bath cooled by dry ice and maintained at -10 ± 1°C. A styrofoam container was used to hold the hot or cold water bath and the reaction vessel.

C.   EXPERIMENTAL PROCEDURES

The normal procedure for a typical experiment was as follows. A 2 percent solution of the hydrazine fuel to be used, either freshly prepared or from stock, was placed in the reaction vessel with the stirring bar. The volume of solution used in Phase 1 depended in general on the experiment, but was usually 500 mL. During Phase 2, the volume was always 50 mL. The addition funnel was put in place and the desired amount of bleach solution placed into the funnel. The gas buret was filled with water and clamped in place. The tubing connections were then made and checked to see that they were tight. The bleach solution was then added, with gentle stirring, at a rate of approximately 3-5 mL/min. Addition at a faster rate was found to

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significantly increase the temperature of the reaction mixture because of the high exothermicity of the neutralization reaction. When the desired quantity of bleach had been added, the reaction was stopped. After a short time, the reaction mixture was poured through a glass wool plug into a large separatory funnel for extraction and further workup.

The final water level in the gas buret was recorded, along with the water temperature and the difference in water levels inside and outside the buret. The barometric pressure was measured with a mercury barometer and recorded. The volume of gas inside the buret was obtained from the buret calibration data, and the pressure of the gas inside was corrected for the vapor pressure of water and for the difference in water levels. The number of moles of gas was then computed using the ideal gas law.

Hydrazine fuels are known to readily absorb carbon dioxide (CO_2) from the air. To examine the effect of carbon dioxide on the reaction products, carbon dioxide was added to the system in a series of experiments before neutralization with bleach. In these cases, the desired quantity of fuel was pipetted into a screw-top test tube and weighed. The desired amount of carbon dioxide in the form of dry ice was added to the test tube, which was then reweighed. The contents of the test tube were then flushed with the appropriate amount of HPLC-grade water into the reaction vessel and the experiment conducted as described above.

Several experiments were conducted using solid bleach instead of the usual liquid bleach. To avoid excess heat generation, the solid bleach was mixed with enough water to form a solution with the same hypochlorite concentration as in the liquid bleach. Some or all of the inert ingredients in the solid bleach were found to be insoluble. Nevertheless, the entire mixture was used in the neutralization experiment, with the insoluble material added along with the solution in the usual way.

As mentioned earlier, some experiments were conducted at temperatures different from ambient. Other than to thermostat the reaction vessel, no change in procedure was made for the high-temperature runs. For the cold-temperature runs, however, the fuel solution also contained 12 percent methanol to serve as an antifreeze (Reference 25). Corresponding control runs were also made at room temperature with 12 percent methanol (CH_3OH) solutions.

The stock 2 percent fuel solutions were alkaline. Measurements of the solution pH gave values of 10.2 for hydrazine and approximately 10.5 for the other fuels. Several runs were also conducted at pH values near 2.0, adjusted to this value by the addition of 0.1 M sulfuric acid.

One UDMH run was conducted using "reverse addition." In this procedure, the bleach was placed in the reaction vessel at the start of the experiment and the desired quantity of fuel solution added using the addition funnel. Other procedures were unchanged.

Two types of experiments were used to verify that atmospheric oxygen was not responsible for a significant number of the reaction products. The first, conducted only for UDMH, involved considerable effort to exclude room air from the reaction system. The apparatus was thoroughly flushed with nitrogen, and both the fuel and bleach solutions were carefully sparged with nitrogen before use. The bleach solution was kept under a blanket of nitrogen during the experiment; this precaution was unnecessary for the fuel solution in the reaction vessel.

The second type of experiment may be regarded as a blank run. In these experiments, all procedures were followed as usual except that aerated HPLC-grade water was added to the fuel solution instead of bleach.

D. ANALYTICAL PROCEDURES

1. Sample Preparation

Dichloromethane was used to extract the organic reaction products from the final aqueous reaction mixture. The organic extract was then dried over anhydrous sodium sulfate before analysis by gas-chromatography/mass-spectrometry (GC/MS). For quantitative GC/MS analysis, tridecane ($C_{13}H_{28}$), was added to the extracts as an internal standard at a concentration of 50 μg of tridecane per mL of the extract. Before analysis, extracts were stored at -10°C in vials sealed with Parafilm®. No analysis was made for the constituents that remained in the aqueous phase, nor was the evolved gas subjected to analysis.

2. Standards Preparation

A stock solution of tridecane (99 percent purity, Aldrich Chemical Co.) was prepared in hexane at a concentration of 5 mg/mL. Stock solutions of NDMA, NEMA, and NDEA were prepared in hexane at a concentration of 1 mg/mL. The nitrosoamines were obtained from Sigma Chemicals Co. in 100-mL vials containing 100 mg of the compound, and the hexane was added directly to these vials. To obtain data for a calibration curve, five solutions of NDMA were prepared at concentration of 20, 40, 80, 120, and 200 μg/mL in dichloromethane. Fifty micrograms of tridecane was then added to each as an internal standard. Peaks for each nitrosoamine and the internal standard were identified in the total-ion chromatogram of the standard solutions, and the areas were calculated using the computer software available with the GC/MS instrument. A calibration curve was constructed only for NDMA. Standard solutions of the hydrazines for impurity analysis were prepared by adding 50 μL of the hydrazine to 10 mL of dichloromethane. The instrument detection limit for NDMA was determined to be 0.3 μg/mL of extract. This limit corresponds to approximately 0.08 μg/mL of reaction mixture. The detection

limits for NEMA and NDEA were not determined but are expected to be very close to this value, based on their relative instrument response factors.

3. Instrumentation

Mass spectra were obtained using a Hewlett-Packard gas-chromatograph/mass-spectrometer (Model No. 5984) equipped with the Speed software. Gas chromatography was performed using a 60 m by 0.32 mm I.D., 1-μ film thickness DB-1 (J & W Scientific) fused silica column. The carrier gas was helium at a column head pressure of 19 psi and a linear velocity of 50 cm/s at 20°C. The GC temperature program used was: hold at 10°C for 2 minutes, then increase the temperature at 4C°/min to 260°C, and hold for 10 minutes. All sample injections were 2 μL in volume and were made in the splitless mode (splitter valve closed for 0.4 minutes). The injector temperature was maintained at 280°C.

The GC column was coupled directly to the ion source of the mass spectrometer. The quadrupole mass spectrometer was placed in the electron impact mode. Electron impact ionizing energy was 70 eV; source temperature was 170°C.

During Phase 1, infrared spectra of some reaction products were obtained using gas chromatography/Fourier transform infrared spectroscopy (GC/FTIR). The instrument used was a Nicolet 60 5X with TMON 1.5 software. The GC and GC column were identical to those used in the GC/MS analyses and were operated in the same manner.

SECTION III

RESULTS AND DISCUSSION

A. FUEL ANALYSES

Samples of the anhydrous hydrazine, MMH, and UDMH used in this work were analyzed for organic impurities before use in neutralization experiments. No quantification of fuel impurity levels was attempted. The only organic impurity found in the sample of hydrazine was aniline, a substance already known to be present in anhydrous hydrazine at the 0.3-0.5 percent level (Reference 1). Aniline is used in the process by which the final amount of water is removed.

Three impurities were found in the MMH sample: chloromethane (CH_3Cl) and formaldehyde N-methylhydrazone, and at a much lower level, formaldehyde N-ethylhydrazone. The latter two identifications were postulated, based on their mass spectra; the identification of chloromethane was confirmed from its published mass spectrum (References 36,37). That the chloromethane peak was not simply a solvent impurity was verified by GC/MS analysis of the dichloromethane solvent alone. During Phase 2 of the program, a fresh sample of MMH was obtained and analyzed. This new sample was found not to contain the two hydrazone impurities listed above. Chloromethane was still a minor impurity.

Analysis of the UDMH sample using GC/MS and GC/FTIR spectroscopy yielded a total-ion chromatogram with two major, three smaller, and six much smaller peaks, in addition to those due to the solvent and the UDMH itself. The two major impurities were unambiguously identified as dimethylamine from its published mass spectrum (References 36,37), and formaldehyde N,N-dimethylhydrazone from its published infrared spectrum (Reference 38). One of the intermediate peaks was also unambiguously found to be chloromethane. The remaining intermediate peaks were postulated to be formaldehyde N-methylhydrazone and formaldehyde N,N-methylethylhydrazone, based on their mass spectra. The remaining minor impurities could not be identified.

The chemical natures of the trace impurities found in the MMH and UDMH samples are, for the most part, understandable. The hydrazones are partial oxidation products of the bulk substance. The dimethylamine found in the UDMH sample is one of the reagents from which UDMH is synthesized using the Raschig process (Reference 1). The origin of the chloromethane is unclear; because it was found in all the methylated fuel samples, it is presumably a residual from some common step in the manufacturing process for MMH and UDMH.

B. GENERAL REACTION PRODUCT ANALYSES

The main purpose in carrying out neutralization experiments was to obtain samples of the reaction product mixtures produced, using the four different fuels under conditions that reasonably simulated an actual "field" neutralization of a hydrazine spill. In addition, the progress of the reaction was observed and, when feasible, the number of moles of gas evolved during the reaction was estimated. The ratio of the number of moles of gas evolved to the initial number of moles of fuel used is a measure of the extent to which the neutralization reaction goes to "completion." A summary of the neutralization experiments performed during Phase 1 is given in Table 1, and a summary of the experiments performed during Phase 2 is given in Table 2. Quantitative nitrosoamine results are presented in Section C.

TABLE 1. SUMMARY OF PHASE 1 NEUTRALIZATION EXPERIMENTS

Experiment No.	Substance	Initial Concentration (percent)	Bleach[a]	Mole Ratio to Initial Moles Fuel			Nitrosoamines Found
				ClO^-	Gas	Added CO_2	
1	N_2H_4	2.0	L	2.23	1.04	-	No
2	"	2.0	L	2.11	b	0.36	No
3	"	2.0	L	2.19	0.95	-	No
4	"	2.0	S	2.22	1.0[c]	-	No
5	MMH	1.7	L	2.21	0.67	-	Yes
6	"	1.7	L	2.09	0.78	-	Yes
7	"	1.8	L	2.20	d	0.33	No
8	"	1.8	S	2.22	0.92[c]	-	Yes
9	UDMH	1.6	L	2.77	<0.04	-	Yes
10	"	3.2	L	2.18	0.1	-	Yes
11	"	1.6	L	2.26	<0.01	0.10	No
12	"	1.6	L	2.27	0.17	-	Yes
13	"	1.6	S	2.95	0.30	-	Yes
14	"	1.6	L	2.80	0.17	-	Yes
15	AE-50	3.5	L	2.23	d	-	Yes
16	"	1.8	L	2.64	d	-	Yes
17	"	1.8	L	2.65	d	0.29	Yes
18	"	1.8	L	2.80	d	-	Yes
19	"	1.8	S	2.68	d	-	Yes

[a] L = liquid; S = solid bleach.

[b] Leak in gas collection system.

[c] Estimates from the amount of bleach added at cessation of gas evolution.

[d] Quantity of gas evolved exceeded capacity of gas buret.

TABLE 2. SUMMARY OF PHASE 2 NEUTRALIZATION EXPERIMENTS

Experiment No.	Substance	Initial Concentration (percent)	Mole Ratio to Initial Moles Fuel		Comment[b]
			ClO^{-a}	Gas	
1	N_2H_4	2.0	2.4 (2.2)	0.91	
2	"	2.0	2.8 (2.1)	0.78	12% CH_3OH
3	"	2.0	3.0 (2.4)	0.75	12% CH_3OH
4	"	2.0	2.8 (2.2)	0.73	pH = 2.1
5	"	2.0	2.8 (2.2)	0.85	T = -10°C
6	"	2.0	2.8 (2.2)	0.91	T = 47°C
7	MMH[c]	1.7	8.1 (1.2)	1.6	
8	"	1.7	4.5 (1.4)	1.7	
9	"	1.7	7.3 (1.2)	0.79	old MMH
10	"	1.7	2.1 (1.6)	1.5	12% CH_3OH
11	"	1.7	8.5 (2.2)	1.4	old MMH, 12% CH_3OH
12	"	1.7	5.9 (1.3)	1.4	old MMH, 12% CH_3OH
13	"	1.7	3.3 (2.6)	0.72	pH = 1.8
14	"	1.7	2.7 (1.3)	1.7	T = -10°C
15	"	1.7	3.3 (1.5)	1.5	T = 44°C
16	UDMH	1.6	5.1 (-)	0.09	
17	"	1.6	5.7 (3.0)	0.23	
18	"	1.6	5.7 (-)	0.52	Reverse addition
19	"	1.6	8.5 (-)	0.0	12% CH_3OH
20	"	1.6	11.3 (4.9)	0.56	pH = 1.4
21	"	1.6	5.0 (4.5)	0.70	pH = 2.1
22	"	1.6	4.0 (-)	0.02	T = -10°C
23	"	1.6	5.7 (-)	0.0	T = 44°C
24	AE-50	1.8	10.0 (2.5)	0.54	
25	"	1.8	5.0 (2.5)	0.66	12% CH_3OH
26	"	1.8	3.5 (3.2)	0.81	pH = 2.0
27	"	1.8	5.2 (2.6)	0.67	T = -10°C
28	"	1.8	4.9 (2.6)	0.29	T = 45°C

[a]Final ratio. Values in parentheses indicate value at cessation of gas evolution (A dash indicates that this could not be estimated.) All experiments used liquid bleach (5.25% NaClO).

[b]Nitrosoamine results are given in Tables 3-5.

[c]All runs except these specifically indicated used the second MMH sample.

Table 3 gives a partial list of products from neutralization experiments on all three methylated fuels. Only those products that have been confirmed by comparison of their mass spectra or infrared spectra with published spectra are listed. In most cases, most reaction products could not be identified, including many major ones. A very approximate indication of the peak size for each substance for a normal run is also given in Table 3; the actual product distribution in any particular run depends upon many factors, as discussed below.

Certain other apparent reaction products were identified and confirmed but are not included in Table 3. These substances are believed to be formed from reactions involving cyclohexene, which is present as an impurity at part-per-million levels in the dichloromethane used in the extractions, and reactive species present in the final reaction mixture. All such products were found only at very low levels. These products included 2-H-pyran, 3,4-dihydro; 1-cyclopropyl ethanone; 2,3-dihydro-3-methyl furan; 2,4-pentanedione; 4-heptanone-dimethylhydrazone; and 2-propenal, 3-dimethylamino-3-(1-methylethyl) amine.

TABLE 3. CONFIRMED PRODUCTS FROM THE HYPOCHLORITE
NEUTRALIZATION OF METHYLATED HYDRAZINE FUELS[a]

	Fuel		
Substance	MMH	UDMH	AE-50
Formaldehyde dimethylhydrazone	S	M[b]	M
Chloroform	M	M	M
Carbon tetrachloride	-	S	-
Acetaldehyde, ethylidene hydrazone	-	S	-
N,N-dimethylformamide	-	M	M
Dimethylnitrosoamine	-	L	M
Ethylmethylnitrosoamine	M	-	M
Diethylnitrosoamine	M	-	-
Dimethylcyanamide	-	M	M
5-methyl-2,4-dihydropyrazole-3-one	M	M	M
Isoxazolidine	-	S	-
1-methyl-1,2,4-triazole	S	M	M

[a]S = small peak; M = medium peak; L = large peak.
 Peak size indicated for typical normal runs; product
 distribution varies with experimental conditions. In
 most cases, several major products could not be
 identified.

[b]A very large peak in one early run in Phase 1.

1. -Hydrazine

The reaction of hypochlorite with hydrazine was quite rapid. During Phase 1, the mole ratio of gas evolved to initial fuel was 1.0 ± 0.05. During Phase 2, the gas yield seemed to decrease somewhat to 0.9 for a normal run and to about 0.75 for runs containing methanol or at low pH. Except for the runs involving carbon dioxide and at low pH, the general course of the reaction was quite consistent. The reaction mixture remained colorless while gas continued to be evolved, but turned pale yellow immediately after the evolution of gas was complete, indicating that hypochlorite reacts much more rapidly with hydrazine than with aniline. As soon as the hydrazine is fully consumed, the aniline reacts to give colored reaction products. GC/MS analysis of the dichloromethane extract, which contained all the colored products, showed that the aniline was fully consumed, but the only indication of the reaction products was a small peak (molecular weight = 167) at a retention time of 56 minutes. Use of solid bleach instead of liquid resulted in the disappearance of the small peak at 56 minutes, with no peaks appearing.

If carbon dioxide is added to the hydrazine, or if the hydrazine solution is made acidic by the addition of mineral acid prior to dilution and neutralization with liquid bleach, the evolution of gas remains vigorous, but the color changes are distinctly different. The reaction mixture gradually turns a beige or champagne color as bleach is added, up to the endpoint (cessation of gas evolution). The addition of bleach beyond that point causes the solution to quickly turn bright yellow. The color then changes to a distinctly different yellow-green color within two to three minutes. The yellow-green color fades at a noticeable rate until, after three hours, the solution is essentially clear and colorless. At no time is the intensity or tint of the observed color such that it could be due simply to a dilute bleach solution.

GC/MS analysis of the extract from the excess carbon dioxide experiment yielded a total-ion chromatogram containing only two relatively minor peaks in addition to the usual solvent peaks (the solvent contains minor impurities). These two substances have not been identified, but are believed to be reaction products of the aniline impurity.

No products of the hydrazine-hypochlorite neutralization reaction were detected, but none were expected because the analytical procedures were designed to investigate organic reaction products. The gas yield results for hydrazine suggest that the reaction goes essentially to completion, with the production of one mole of nitrogen gas and two moles of chloride ion per mole of hydrazine. Ammonia is another possible oxidation product (Reference 1), and the less-than-stoichiometric yield of gas, presumed to be molecular nitrogen, in some experiments may be explained by the formation of a small amount of ammonia. As indicated earlier, no analyses were carried out for major inorganic constituents of the final reaction mixture.

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2. Monomethylhydrazine

The reaction of hypochlorite with MMH does not go to completion, and a large number of oxidation products form. The measurements of gas evolution are somewhat contradictory. During Phase 1, 0.72 ± 0.05 moles of gas were evolved per mole of MMH in normal runs, and 0.92 moles/mole MMH in the run using solid bleach. During Phase 2, however, the gas/fuel mole ratio ranged from 1.4 to 1.7. The only exceptions were one normal run using the same MMH sample as that used in Phase 1, for which the ratio was 0.79, and the run at pH = 1.8, for which the ratio was 0.72. Both MMH samples gave essentially the same gas/fuel ratio, 1.4-1.5, in the presence of 12 percent methanol.

During the course of the reaction, the solution gradually turns yellow as bleach is added. Nothing appears to happen when excess bleach is added beyond the endpoint. The color persists if the mixture is allowed to stand, and extraction with dichloromethane results in most but not all of the colored material being transferred to the organic phase. Both phases show yellow, with no difference in tint. Back extraction of the organic layer with water yielded a yellow aqueous phase, in addition to the yellow organic layer. Addition of excess carbon dioxide had no effect on the color changes observed during the reaction.

The use of solid bleach produced no difference in the course of the reaction until the end. As with the experiments on MMH using liquid bleach, the solution was yellow immediately after adding the final amount of bleach. However, in this case the reaction mixture turned completely colorless during the next one and one-half hours. The sediment, presumably silica or alumina, may catalyze the further decomposition or reaction of some of the reaction products.

In Phase 1, chloroform was identified as a significant reaction product, based on GC/MS analysis of the extract of the liquid bleach reaction mixture. In addition, although individual components were not quantified, the largest single peak in the total-ion chromatogram corresponded to NEMA, and another large peak corresponded to NDEA. These identifications were based on the comparison of both the infrared and mass spectra of NDEA with published spectra (References 36,37) and of the mass spectrum of NEMA with a published spectrum (Reference 36). The infrared spectrum of the latter compound was obtained and is completely consistent with this identification. Several other major products, some of them chlorinated, could not be identified. Over 100 peaks were found in the total-ion chromatogram.

Analysis of the MMH/solid-bleach reaction mixture showed far fewer peaks (approximately 30 of all sizes), and those found were generally much smaller. Most remain unidentified. At least two significant new and as yet unidentified peaks were found. Small quantities of NEMA and NDEA were also found, as was chloroform.

Carbon dioxide also substantially reduced the number of products formed. Most of these compounds are new, and most seem to be multiply chlorinated. The largest peak may correspond to the methylhydrazone of phosgene (dichloroformaldehyde), but confirmation is required. In the carbon dioxide experiment, no nitrosoamines were found.

In Phase 2, the GC/MS analysis of MMH neutralization products resulted in total-ion chromatograms with far fewer peaks in general than in Phase 1. Chloroform was still a significant product under all conditions, and both NEMA and NDEA were detectable except as noted below. Other products could not be identified, but at least one doubly chlorinated major product of apparent molecular weight 176 was sufficiently unstable that it disappeared from the dichloromethane extract on storage over an extended time in a freezer. Aging the reaction mixture for seven days also resulted in a significant decrease in that unknown substance and carbon tetrachloride appeared. Increasing the amount of bleach by a factor of about 2.4 also resulted in a significant reduction in the yield of the same unknown substance, but had only minor effects on other products. At a pH of 1.8, the total-ion chromatogram was much cleaner. No nitrosoamines were detected, and the unknown discussed above was still present, but to a lesser degree. A generally higher degree of chlorination than in the products from normal runs was observed. Aging had essentially no effect on the acidified reaction mixture. The product mixtures from runs at -10°C and 44°C were very similar to those obtained at room temperature, except that no nitrosoamines were produced at -10°C. At room temperature, the presence of methanol gave rise to several new unknown substances.

3. Unsymmetrical Dimethylhydrazine

The reaction between hypochlorite and UDMH yields much less gas per mole of fuel than is the case for MMH, with the balance remaining in solution in the form of incompletely oxidized reaction products. The yield seems to depend somewhat on the rate at which hypochlorite is added to the dilute fuel solution and possibly on the initial fuel concentration. Both the yield of gas and the overall product distribution are somewhat difficult to reproduce.

During the course of the neutralization, the reaction mixture becomes yellow, then orange, and then red-brown. The dark red-brown color fades with further addition of hypochlorite, although gas continues to evolve. Extraction with dichloromethane yields a yellow aqueous phase and a dark yellow or orange organic layer. Back extraction with water also yields a yellow water layer. The addition of excess carbon dioxide has no obvious effect on the course of the reaction.

The use of solid bleach produced no visual difference in the course of the reaction although, as discussed later, the product distribution was different. In this case, the reaction mixture was extracted with dichloromethane immediately after neutralization. Substantially more gas was

produced (0.32 ± 0.05 moles/mole fuel), and the sediment may catalyze the gas-producing reaction.

In the Phase 1 experiments, GC/MS and GC/FTIR analysis of the reaction mixture revealed 90-100 compounds. The major reaction product was formaldehyde N,N-dimethylhydrazone, identified from its infrared spectrum (Reference 38) and its mass spectrum (Reference 36). Other confirmed reaction products were NDMA, N,N-dimethylcyanogen (relatively minor), N,N-dimethylformamide (relatively minor), and chloroform (minor). Two nearby peaks, one major and one relatively minor, both having apparent molecular weights of 86, have been tentatively identified as acetaldehyde N,N-dimethylhydrazone, and formaldehyde N,N-methylethylhydrazone, respectively, based on their mass spectra. No other nitrosoamines were detected. Several other major products and most of the minor products remain unidentified. One unidentified major peak, having a relatively short retention time, may be chlorinated UDMH. This peak disappeared from the extract with time and has an appropriate molecular weight. Other changes in the distribution of reaction products in the dichloromethane extract also occurred over time.

The use of solid bleach had a very noticeable effect on the reaction products. The main product, present in a very large amount, does not appear at all in the liquid bleach extract and has been tentatively identified as sym-tetrahydro-1,2,3,5-tetramethyltetrazine, the dimer of formaldehyde N,N-dimethylhydrazone, based on infrared and mass spectra. Confirmed reaction products are chloroform, formaldehyde N,N-dimethylhydrazone (major), NDMA, N,N-dimethylcyanogen (minor), and N,N-methylethylhydrazone (minor). Other postulated products are formaldehyde N-methylhydrazone, formaldehyde N,N-methylethylhydrazone, and acetaldehyde N,N-dimethylhydrazone, all of which are minor products. Several major products remain unidentified. In general, more high-molecular-weight products are formed with solid bleach than with liquid bleach. A total of 75-80 peaks were seen in the total-ion chromatogram.

Addition of carbon dioxide before neutralization with liquid bleach also had a significant effect on the reaction products. Between 65 and 70 peaks were seen in the total-ion chromatogram. Confirmed products are formaldehyde N,N-dimethylhydrazone (major), N-N-dimethylcyanogen (minor), and N,N-dimethylformamide (minor). Again, several major and most minor reaction products could not be identified. One major product is tentatively identified as sym-tetrahydro-1,2,4,5-tetramethyltetrazine, the dimer of formaldehyde N,N-dimethylhydrazone and the major product when solid bleach was used. Very few products seem to be chlorinated, in contrast to the MMH case. This difference may be due to the fact that only 0.1 mole carbon dioxide was added per mole of fuel, as opposed to nearly 0.3 mole in the MMH case. Although a careful search was made, no nitrosoamines were found in the excess carbon dioxide reaction mixture.

As was the case for MMH, the neutralization experiments in Phase 2 yielded total-ion chromatograms with significantly fewer peaks and generally lower by-product concentrations. As in Phase 1, the product distribution was

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somewhat difficult to reproduce. Chloroform was almost always a significant product. Carbon tetrachloride was observed as a significant product with a hypochlorite/fuel ratio equal to 4.57, a very minor product with a hypochlorite/fuel = 5.72, and not present at all with hypochlorite/fuel = 9.9. Other changes in relative peak heights were also observed on varying the quantity of bleach added. NDMA was produced under almost all conditions. Neutralization of an acidic solution yielded many new peaks, all singly or multiply chlorinated, and all unidentifiable. No nitrosoamines were found in the acidic run. Product mixtures from the reverse addition run and the run at 44°C were very similar to those of the normal-room-temperature runs, but significant differences appeared in the run carried out at -10°C. Some products were missing, new ones were present, and the relative amounts of others were different. Again, most substances could not be identified. The product distribution from the room temperature run in the presence of methanol was quite similar to that of the cold temperature run. Aging a normal reaction mixture at room temperature for up to two weeks resulted in some noticeable changes in the product distribution, but did not result in a substantive reduction in the overall concentration of by-products.

4. Aerozine-50

The course of the reaction with liquid bleach is similar to that of the UDMH/liquid-bleach reaction, except that the colors are somewhat less intense, because only about 35 percent as much UDMH is present on a molar basis. No obvious color changes due to the presence of aniline were seen. In Phase 1, analysis of the dichloromethane extract of the final reaction mixture yielded a total-ion chromatogram with only 30 peaks, most quite small. The major confirmed product was chloroform, and no formaldehyde N,N-dimethylhydrazone was detected, although the substance tentatively identified as its dimer was seen as a significant reaction product. A small amount of NDMA was also found, as were small amounts of N,N-dimethylcyanogen and N,N-dimethylformamide.

When solid bleach was used, the course of the reaction was the same as before except near the end of the experiment, when the final color was a brighter yellow. Also, the final color faded to a colorless solution over a five-minute period with the evolution of more gas; again, the sediment seems to catalyze further changes in the reaction mixture. Approximately the same number of peaks was seen in the total-ion chromatogram as when liquid bleach was used. Again, the major product is chloroform, and small quantities of NDMA, N,N-dimethylcyanogen and N,N-dimethylformamide were found. Other significant products could not be identified.

When carbon dioxide was added before neutralization with liquid bleach, a rose color developed with the first addition of bleach. After further addition, this color faded and the solution became yellow. The yellow color intensified throughout the experiment until approximately 80 percent of

the total amount of bleach had been added. Further addition of bleach yielded no more gas, but the color faded from a deep orange to yellow, and the tint of the yellow also changed. The final color faded slowly; the organic extraction layer was yellow and the aqueous layer a very faint yellow color. Analysis with GC/MS indicated that the major product was chloroform and that small amounts of NDMA, N,N-dimethylcyanogen, and N,N-dimethylformamide were also formed.

In Phase 2, the number and overall concentration of by-products were smaller than observed in Phase 1, and most could not be identified. The products were for the most part the same as those in the UDMH runs. The effects of aging the reaction mixture and of the addition of more bleach were noticeable but not dramatic. No general reduction in the concentration of by-products occurred. Carbon tetrachloride was seen as a minor product in the acidic run, and most other products were also singly or multiply chlorinated. The run at 44°C yielded results very similar to those of the room temperature run. Both the low-temperature run and the room temperature run in the presence of methanol yielded many more peaks in the total-ion chromatogram than did the normal room temperature run, and the two chromatograms were quite similar in most respects, as was the case for UDMH.

C. NITROSOAMINE ANALYSES

As indicated in the discussion of scope in the introduction, the emphasis in Phase 2 of this work was placed on the quantification of the levels of the different nitrosoamines found under different conditions as reaction products of the hypochlorite neutralization of the various methylated hydrazine fuels. Table 1 provides a qualitative indication of the presence or absence of nitrosoamines in the reaction mixtures from the Phase 1 experiments.

1. Monomethylhydrazine

As Table 4 shows, part-per-million amounts of both NEMA and NDEA were produced under most conditions; no NDMA was detected in any experiment. The effect of adding different quantities of hypochlorite is illustrated by Run 1 and Run 2, Samples 1 and 2. As the ratio of hypochlorite to fuel increases from 1.9 to 4.5 to 8.1, the observed levels of both NEMA and NDEA decrease progressively to below the detection limit. Aging the final reaction mixture by seven days had very little effect on the NEMA level, but resulted in a noticeable decrease in the NDEA level, as can be seen from the results of Run 2, Samples 2 and 3. As the results of Run 3 show, when the pH is adjusted to very acidic levels before neutralization, no nitrosoamines could be detected in the reaction mixture.

TABLE 4. NITROSOAMINE LEVELS FROM THE MMH/HYPOCHLORITE REACTION[a]

Run	Conditions	Sample	Moles ClO⁻/ Moles Fuel	Nitrosoamine Concentrations (ppm)		
				NDMA	NEMA	NDEA
1	Normal	1	8.1	-	-	-
2	Normal	1	1.9	-	4.9	2.1
		2	4.5	-	2.1	1.5
		3[b]	4.5	-	2.1	0.8
3	pH = 1.8	1	3.3	-	-	-
4	T = 44°C	1	3.3	-	6.0	2.7
5	T = -10°C	1	2.7	-	-	-
6	12% CH₃OH	1	2.1	-	6.1	1.7
7	Blank	1	0.0	-	-	-

[a]Unless otherwise noted, all samples were extracted from the reaction mixture within one hour of the completion of the reaction. A dash implies no nitrosoamine was detected.

[b]After aging seven days.

The effect of temperature is illustrated by the results from Runs 4 and 5. High temperatures seem to promote the production of nitrosoamines from MMH, whereas low temperatures seem to have the opposite effect. In fact, no nitrosoamines could be detected at all in the reaction mixture from the -10°C run. The effect of the presence of methanol can be seen by comparing Runs 2, 5, and 6. At room temperature, the presence of 12 percent methanol seems to cause an increase in the level of nitrosoamines produced. Because the low-temperature Run 5 also had 12 percent methanol present, the lack of any observable nitrosoamines in that run is somewhat surprising.

Finally, a blank run was carried out in which HPLC-grade water was added instead of bleach to the two percent fuel solution. The final mixture was analyzed in the usual way. The absence of any detectable oxidation products, including nitrosoamines, indicates that air oxidation is not responsible for any of the products observed in the other runs and that such products are entirely the result of the hypochlorite reaction.

It is also convenient at this point to recall that in the Phase 1 experiments using MMH, both NEMA and NDEA were found in all cases, except the run in which carbon dioxide was added to the system. This result is probably due to the effect of the carbon dioxide on the pH of the solution, although the pH of the initial solution was not actually measured in this case.

2. Unsymmetrical Dimethylhydrazine

Table 5 shows the results from the UDMH neutralization experiments. In most experiments, part-per-million levels of NDMA were produced, the sole exceptions being the blank run, in which no bleach was added, and the run at low pH. In Run 7, the 2 percent UDMH solution was added dropwise to bleach rather than the other way around, and a significant amount of NEMA was formed. This was the only run in which a nitrosoamine other than NDMA was definitely observed. In three other samples, two from Run 1 and one from Run 4, very small peaks were detected in the GC/MS total-ion chromatograph at or very near the same retention time as NEMA. Mass spectrometric analysis was inconclusive regarding the identity of the substance or substances producing the peak, but the presence of a very small amount of NEMA could not be ruled out.

TABLE 5. NITROSOAMINE LEVELS FROM THE UDMH/HYPOCHLORITE REACTION[a]

Run	Conditions	Sample	Moles ClO⁻/ Moles Fuel	Nitrosoamine Concentrations (ppm)		
				NDMA	NEMA	NDEA
1	Normal	1	5.1	5.3	d	–
		2	9.9	6.5	d	–
		3[b]	5.1	3.2	–	–
		4[b]	9.9	0.8	–	–
2	Normal	1	1.2	49.2	–	–
		2	4.6	8.1	–	–
		3[b]	4.6	2.6	–	–
		4[c]	4.6	3.0	–	–
3	pH = 2.1	1	5.0	–	–	–
4	T = 44°C	1	5.7	7.3	d	–
5	T = -10°C	1	4.0	7.0	–	–
6	12% CH₃OH	1	8.5	11.0	–	–
7	Reverse addition	1	5.7	6.9	3.6	–
8	Oxygen free	1	7.1	3.8	–	–
9	Blank	1	0.0	–	–	–

[a]Unless otherwise noted, all samples were extracted from the reaction mixture within one hour of the completion of the reaction. A dash implies no nitrosoamine was detected.

[b]Extracted after aging the reaction mixture for 7 days.

[c]Extracted after aging the reaction mixture for 14 days.

[d]Possible small amount coeluting with another compound.

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The effect of adding different quantities of bleach is illustrated by Runs 1 and 2. Relatively large amounts of NDMA are produced by the time the neutralization is approximately half finished, as Sample 1, Run 2, shows. By the time the hypochlorite/fuel mole ratio approaches five, the amount of NDMA is considerably reduced but is still significant. The addition of additional hypochlorite, up to a hypochlorite/fuel mole ratio of 10, has no further effect.

The effect of aging the final reaction mixture can also be seen in Runs 1 and 2, in which for a hypochlorite/fuel ratio of five or so, the final nitrosoamine level seems to stabilize at about 3 ppm. If, however, the hypochlorite/fuel ratio is near 10, the final nitrosoamine level is significantly reduced, although not completely eliminated.

At a highly acidic pH, no nitrosoamines were detected, which is in agreement with the MMH results discussed above.

As Runs 4 and 5 show, temperature has very little effect on the nitrosoamine levels produced. However, because the low-temperature run also had 12 percent methanol present and because substantially higher nitrosoamine concentrations are produced in the presence of methanol (see Run 6), low temperatures may in fact suppress nitrosoamine formation. Based on the results of Run 6, a substantially higher nitrosoamine level would be expected for Run 5 than was actually observed.

To show that the observed reaction products are due to the hypochlorite-fuel reaction and not to the effect of oxygen from room air, two experiments were conducted. In the first, bleach was added as usual, but considerable effort was made to exclude oxygen from the system and from the solutions used. In the second experiment, no attempt was made to exclude air from the system, but HPLC-grade bottled water was added instead of bleach. The results are shown in Table 4 as Runs 8 and 9, respectively, and it is clear that the effect of air oxidation is negligible under the experimental conditions employed in this work.

As with MMH, NDMA was found in all the Phase 1 experiments listed in Table 1 except the one that involved the addition of carbon dioxide to the system. It is again reasonable to assume that the main effect of carbon dioxide is to acidify the solution.

3. Aerozine-50

Table 6 shows the results from the AE-50 neutralization experiments. In most cases, both NDMA and NEMA were detected at the part-per-million level. Because AE-50 contains only UDMH and hydrazine, the detection of NEMA here, but not in the UDMH runs, is interesting and somewhat unexpected. NDEA was not detected in any AE-50 reaction mixture. As in the UDMH case, the only experiments in which no nitrosoamines were detected were the blank run, in

TABLE 6. NITROSOAMINE LEVELS FROM THE
AE-50/HYPOCHLORITE REACTION[a]

Run	Conditions	Sample	Moles ClO⁻/ Moles Fuel	Nitrosoamine Concentrations (ppm)		
				NDMA	NEMA	NDEA
1	Normal	1	5.1	1.7	12.2	-
		2	10.0	1.0	1.6	-
		3[b]	5.1	1.3	0.5	-
		4[b]	10.0	0.3	0.3	-
2	pH = 2.0	1	3.5	-	-	-
3	T = 45°C	1	4.9	1.9	2.0	-
4	T = -9°C	1	5.2	2.9	c	-
5	12% CH₃OH	1	5.0	2.4	c	-
6	Blank	1	0.0	-	-	-

[a]Unless otherwise noted, all samples were extracted from the reaction mixture within one hour of the completion of the reaction. A dash implies no nitrosoamine was detected.

[b]Extracted after aging the reaction mixture for seven days.

[c]Possible small amount coeluting with another compound.

which no bleach was added, and the low-pH run. The mole fraction of UDMH in AE-50 is 0.348. If the presence of hydrazine had no effect on the reaction products of the UDMH-hypochlorite reaction, one would expect that those reaction products would be present at about 35 percent of the level seen in the corresponding UDMH experiments. That this is approximately what is found for NDMA can be seen from a comparison of the corresponding results in Tables 5 and 6. Some degree of synergism between UDMH and hydrazine is indicated by the presence of NEMA in the AE-50 samples and its absence in the UDMH-only samples.

The effects of adding different amounts of bleach and of aging the final reaction mixture can be seen in the results from the different samples from Run 1. Doubling the amount of bleach has a significant effect on NDMA and has a still greater effect on the NEMA level. Aging the reaction mixture has a relatively small effect on NDMA for a bleach/fuel ratio of five, but is more significant for a bleach/fuel ratio of 10. For NEMA, aging has a more pronounced effect at both bleach/fuel ratios than for NDMA.

The effect of higher temperature is negligible for NDMA, but results in a considerable decrease in the level of NEMA. The effect of lower

temperature is uncertain for NDMA because, as Run 5 shows, the presence of methanol increases the NDMA level. Because the presence of NEMA was uncertain in Runs 4 and 5, one is tempted to conclude that the presence of methanol interfered in some way with the production of NEMA in this system.

A blank run was made for AE-50 just as for the other fuels. The results again indicate that oxidation by atmospheric oxygen was not significant in these experiments.

Unlike the MMH and UDMH cases, a small amount of NDMA was detected in the reaction mixture from the Phase 1 experiment in which carbon dioxide was added to the system. The NDMA was, however, a very minor component.

D. GENERAL DISCUSSION

Although relatively few studies exist of the oxidation by hypochlorite of hydrazine and methylated hydrazines, much work has been done on the nature of the reactive intermediate species produced by the oxidation of these fuels by a variety of other oxidizing agents (Reference 1 and references therein). As a result of these studies, it is possible to explain some of the features seen in the results presented in the previous sections.

The exact mode of the initial attack of hypochlorite on hydrazine or any of its methylated analogs has not been experimentally determined. It is known, however, that the attack of hypochlorite on primary or secondary amines results in the substitution of a proton by chlorine (References 39-41). Perhaps the most fundamental example of this process is the formation of chloramine from ammonia and hypochlorite, the first step in the Raschig synthesis of hydrazine:

$$NH_3 + ClO^- = NH_2Cl + OH^- \tag{1}$$

It seems reasonable to suppose, therefore, that the initial attack results in the formation of a chlorohydrazine:

$$R_1R_2N-NH_2 + ClO^- = R_1R_2N-NHCl + OH^- \tag{2}$$

where R_1 and R_2 denote H or CH_3 in this work. The hypochlorite may exist as HClO or ClO^-, and the hydrazine as a neutral species or in the protonated form, depending on the pH. It is not known precisely which species are involved in the initial attack. The subsequent chemical evolution of the system depends on the fate of the chlorohydrazine formed in reaction (2). Other investigators have proposed similar initial steps in related systems. Overberger and Marks suggested the formation of a 1,1-disubstituted-2-chlorohydrazine as the initial step in the oxidation of 1,1-disubstituted hydrazines with tert-butylhypochlorite (Reference 42), and Cram and Bradshaw proposed the initial formation of RNH-NHBr from RNH-NH$_2$ in alkaline bromine solution (Reference 43).

1. Hydrazine

The most likely fate of chlorohydrazine is the loss of HCl and formation of diazene (HN=NH). Other names that have been used for HN=NH are dimide and diimine.

$$H_2N\text{-}NHCl \rightarrow HN=NH + H^+ + Cl^- \tag{3}$$

The formation of diazene from chlorohydrazine was suggested by Hunig et al. (Reference 44) in their review of the chemistry of diazene. They also discuss the evidence for the two proposed reactions that may describe the fate of diazene in the absence of other substances with which it might react:

$$HN=NH \rightarrow N_2 + H_2 \tag{4}$$

$$2HN=NH \rightarrow N_2 + H_2N\text{-}NH_2 \tag{5}$$

The evidence, which consists of gaseous product data, clearly shows that Reaction (4) occurs to a significant extent only in strongly alkaline solution and that Reaction (5) must, therefore, dominate in the pH range used in this study. The gas evolution data presented earlier are consistent with this expectation in that in no case was the mole ratio of evolved gas to initial hydrazine greater than unity, within experimental error.

As shown in Table 2, the observed gas/fuel ratio for hydrazine was significantly below unity, under some experimental conditions, especially in the presence of methanol and at a highly acidic pH. The reasons for this discrepancy are not completely understood. Nitrogenous products other than molecular nitrogen have often been observed with oxidizing agents other than hypochlorite (Reference 1 and references therein). The oxidation of hydrazine may take place via several different mechanisms, but the most important distinction is the number of electrons transferred in the initial step (References 45-48). Two-electron transfer, such as occurs when hypochlorite is used, results in the exclusive formation of diazene and the subsequent production of a stoichiometric amount of nitrogen. On the other hand, one-electron transfer results in the formation of the N_2H_3 free radical, which may either be oxidized further to diazene or may dimerize to tetrazane, which rapidly decomposes to yield two moles of ammonia and one mole of molecular nitrogen (Reference 48). Dissolved chlorine gas functions as a one-electron oxidizing agent, and significant amounts of ammonia may be obtained using chlorine water to oxidize hydrazine (Reference 30). Furthermore, in aqueous systems, chlorine, hypochlorite, and chloride ion exist together according to the equilibrium (Reference 49):

$$Cl_{2(aq)} + H_2O = HClO + H^+ + Cl^- \tag{6}$$

Because chloride ion is a product of the reaction between hydrazine and hypochlorite, some chlorine will be produced during the neutralization,

depending on the pH. In addition, sodium hypochlorite is produced commercially by the electrolysis of cold, dilute aqueous sodium chloride (Reference 50), and some chloride ion may still be present in the bleach. The presence of chlorine in the reaction mixture would lead to the formation of ammonia. In alkaline or neutral solution, however, not enough chlorine would be present to reduce the quantity of nitrogen by 25 percent as observed in the experiments with methanol present. In addition, at alkaline or neutral pH, hypochlorite reacts rapidly with ammonia to yield nitrogen (Reference 28), and any ammonia produced would simply be oxidized further. The stoichiometric amount of nitrogen would still be produced. In acidic solution, however, it seems possible that at least part of the discrepancy in the gas/fuel ratio for hydrazine may be due to the production of ammonia and its retention in solution.

The explanation for the reduction in the amount of nitrogen produced when methanol is present is unknown. Hypochlorite does oxidize methanol, but under the conditions employed in these experiments, the rate of reaction is quite slow. To demonstrate this, alkaline methanol solution was mixed with liquid bleach and allowed to sit in a stoppered flask. The pH was approximately 10, and the mole ratio of methanol to hypochlorite was 2.45. The initial color of the solution was that of slightly diluted bleach. No decoloration was observed after 24 hours; after approximately 84 hours, the solution was colorless. Because a neutralization experiment required only one to two hours for completion, it does not seem likely that products of the hypochlorite oxidation of methanol interfered in the hydrazine neutralization process. It is also difficult to conceive of any reaction between methanol and the intermediates produced by the hypochlorite-hydrazine reaction.

2. Monomethylhydrazine

The most likely fate of the proposed chlorohydrazine intermediate $CH_3NH-NHCl$ is loss of HCl and formation of methyldiazene ($CH_3N=NH$). Monosubstituted alkyl diazenes of this type have been detected and studied experimentally (References 51 and references therein, 52,53). Methyldiazene itself has been isolated as a yellow solid at liquid nitrogen temperatures (Reference 53), and its bimolecular decomposition rate constant in ethanol at 25°C determined to be 0.030 $M^{-1}s^{-1}$ (Reference 52).

Methyldiazene may react further in at least two distinct ways. Kosower and colleagues (Reference 51) observed the bimolecular decay of monosubstituted diazenes and found that the main products are a hydrocarbon and a 1,2-disubstituted hydrazine, analogous to Reaction (5) for diazene itself:

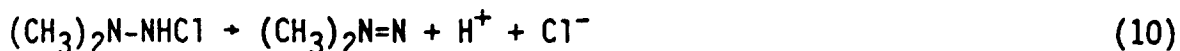$$2CH_3N=NH \rightarrow CH_4 + CH_3NH-NHCH_3 \tag{7}$$

although other unidentified products are also formed. The detailed mechanism for this reaction is not known, but may involve free radicals. In addition, the substituted diazene may be oxidized further by hypochlorite. Although the corresponding rate coefficients are not known, the latter possibility seems the most likely in view of the unexpectedly low value of the bimolecular rate constant for methyldiazene. The following sequence seems reasonable:

$$CH_3N=NH + ClO^- = CH_3N=NCl + OH^- \tag{8}$$

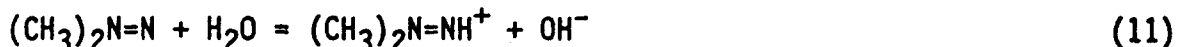$$CH_3N=NCl + H_2O \rightarrow CH_3OH + N_2 + HCl \tag{9}$$

Although no analyses were done in this study for methanol, which is not extracted from water by dichloromethane, methanol was found in 65 percent yield from the chlorinolysis of MMH by Rianda et al. (References 17,18), in support of the above hypothesis. The gas evolution data collected in Phase 1 of this study are also consistent with the assumption that Reaction (8) predominates over Reaction (7), but the large number of other by-products observed suggests that Reaction (9) may not be the only possible fate for 1-methyl-2-chlorodiazene. Complex products would also result from the oxidation of $CH_3NH-NHCH_3$ (symmetric dimethylhydrazine, or SDMH) produced in Reaction (7). The NEMA and NDEA found in the MMH reaction products may arise in this way. The presence of chloroform and other chlorinated products suggests also that one or more reaction paths involve the presence of free radicals. Finally, the gas evolution data collected in Phase 2 imply that nitrogen cannot be the only gaseous reaction product, because the mole ratio of gas evolved to initial MMH was usually greater than unity. In fact, the gas/fuel ratios in the Phase 2 experiments were almost exactly twice the values observed in Phase 1, suggesting that alternative reactions, one leading to twice as much evolved gas as the other, are involved and that for some unknown reason one was predominant during Phase 1 and the other was predominant during Phase 2.
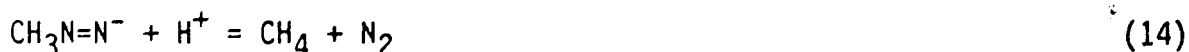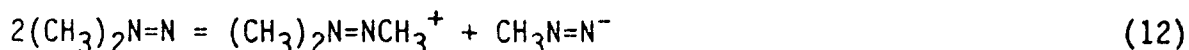
3. Unsymmetrical Dimethylhydrazine

The 1,1-dimethyl-2-chlorohydrazine suggested in Reaction (2) as the likely product of the initial attack of hypochlorite on UDMH is also believed to lose HCl to form a reactive diazene intermediate, but with a somewhat different structure than was the case for hydrazine and MMH:

$$(CH_3)_2N-NHCl \rightarrow (CH_3)_2N=N + H^+ + Cl^- \tag{10}$$
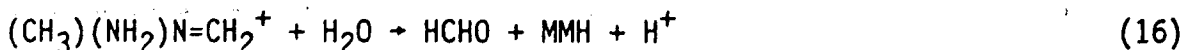
1,1-diazenes of the type shown in Reaction (10) were originally proposed by McBride and coworkers (References 4-6), and their chemistry has been reviewed by Lemal (Reference 54). In aqueous solution, the following equilibrium is also present (Reference 54):

$$(CH_3)_2N=N + H_2O = (CH_3)_2N=NH^+ + OH^- \tag{11}$$

Because of the structural difference between 1,1-disubstituted diazenes and the diazenes previously considered, their respective chemistries are significantly different. A common oxidation product of UDMH is tetramethyltetrazene TMT, $(CH_3)_2NN=NN(CH_3)_2$ (References 4,15,54), but this substance was not found in our study. TMT is formed by the direct, bimolecular dimerization of 1,1-dimethyldiazene and is a major product when the diazene is produced in significant concentrations. At lower concentrations, other reaction pathways are favored over dimerization, with formaldehyde dimethylhydrazone $(CH_3)_2N-N=CH_2$ (FDH) often observed as a major product, as it was in this study. At least two possible mechanisms have been proposed in the literature whereby FDH may be produced by the oxidation of UDMH. Mathur and Sisler (Reference 16) suggested the following reaction sequence:

$$2(CH_3)_2N=N = (CH_3)_2N=NCH_3^+ + CH_3N=N^- \tag{12}$$

$$(CH_3)_2N=NCH_3^+ = FDH + H^+ \tag{13}$$

$$CH_3N=N^- + H^+ = CH_4 + N_2 \tag{14}$$

In aqueous systems, instead of Reaction (14), the species $CH_3N=N^-$ might hydrolyze to give methyldiazene and a hydroxyl ion. An alternative explanation is that suggested by Banerjee et al. (Reference 19):

$$(CH_3)_2N=NH^+ = (CH_3)(NH_2)N=CH_2^+ \tag{15}$$

$$(CH_3)(NH_2)N=CH_2^+ + H_2O \rightarrow HCHO + MMH + H^+ \tag{16}$$

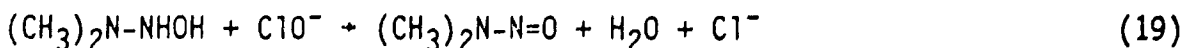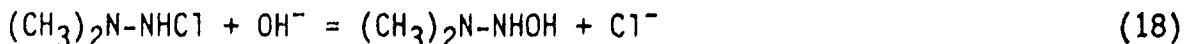$$UDMH + HCHO \rightarrow FDH \tag{17}$$

Tautomers of the type formed in Reaction (15) are believed to play a significant role in the chemistry of 1,1-diazenes (References 54,55). The formation of a hydrazone from an aldehyde and a hydrazine is well known (References 37,38,56).

The chemistry that determines the ultimate mix of reaction products is quite complex and poorly understood. As with MMH, the presence of chlorinated products may indicate that a free radical mechanism is involved. It may also indicate the involvement of dissolved chlorine, at least at the part-per-million level. The gas evolution results obtained in this study are consistent with the general observation that in many cases production of nitrogen accounts for only a small percentage of the nitrogen originally present in the fuel.
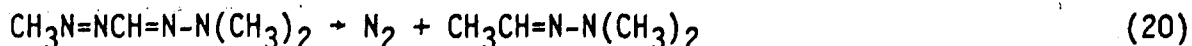
4. Nitrosoamine Formation

The formation of nitrosoamines at the part-per-million level from MMH, UDMH, and AE-50 under most conditions examined constitutes a major finding of this study. The formation of NDMA from UDMH may involve the nucleophilic substitution of the chlorine in 1,1-dimethyl-2-chlorohydrazine by a hydroxyl group, followed by subsequent oxidation of the hydroxyhydrazine by hypochlorite:

$$(CH_3)_2N-NHCl + OH^- = (CH_3)_2N-NHOH + Cl^- \tag{18}$$

$$(CH_3)_2N-NHOH + ClO^- \rightarrow (CH_3)_2N-N=O + H_2O + Cl^- \tag{19}$$

Reaction (18) is analogous to the first step in the hydrolysis of chloramine (Reference 57), and Reaction (19) seems a logical next step in the presence of hypochlorite. This mechanism also explains the observed suppression of NDMA formation in acidic media.

The formation of NEMA and NDEA is not so easy to explain, because it requires the formation of carbon-carbon bonds. One possibility is that nitrogen is split out from, for example, 1,5,5-trimethylformazan to form acetaldehyde dimethylhydrazone, which may undergo further oxidation to give a variety of products:

$$CH_3N=NCH=N-N(CH_3)_2 \rightarrow N_2 + CH_3CH=N-N(CH_3)_2 \tag{20}$$

The formazan has been found in another study as a product of UDMH oxidation in aqueous systems (Reference 19), and acetaldehyde hydrazone was also tentatively identified as a reaction product in Section III. The formation of 1-methylpyrazole from the oxidation of AE-50 also suggests that it was present. At present, the mechanism of NEMA and NDEA formation remains unknown, and the formation of NDEA from MMH but not from UDMH or AE-50 and the formation of NEMA from AE-50 but not UDMH (except for the reverse addition run) also remain unexplained.

The effect of temperature on nitrosoamine formation may be explained as resulting from differing temperature dependences of the rate constants for competing reactions involving nitrosoamine precursors. The observed effect of methanol is not as easy to rationalize. As described in Section II, the presence of methanol seems to cause detectable increases in the yield of nitrosoamines for MMH, UDMH, and AE-50. This effect was also observed by Castegnaro et al. (Reference 3). As discussed above, however, it is difficult to see how methanol becomes involved in the mechanism.

SECTION IV

CONCLUSIONS

As indicated in the introduction, the practical concern that provided the ultimate justification for this work was the need for an environmentally safe and cost-effective method for the disposal of waste hydrazine fuels. The use of an oxidizing agent to "neutralize" the fuel before disposal is a general approach that many research workers have investigated, and hypochlorite bleach is a cheap, strong, easy-to-use oxidizing agent that has been recommended for use with hydrazine fuels. Unfortunately, hypochlorite does not appear to be a suitable neutralizing agent for this type of fuel, with the exception of hydrazine itself, based on the results of this study.

No evidence has been found to indicate that hypochlorite bleach is not an effective and suitable oxidizing agent for hydrazine. Anhydrous hydrazine contains a small amount of aniline, however, and the products of the reaction between hypochlorite and aniline include substances believed to be carcinogenic. The hypochlorite method should not be used for the disposal of hydrazine that contains aniline. In addition, in some circumstances, waste hydrazine may contain other impurities caused by the nature and location of the spill or the manner in which the waste fuel is being stored. In these situations, the use of hypochlorite may lead to undesirable by-products from reactions with these impurities.

Under most experimental conditions, the reaction of hypochlorite with dilute aqueous solutions of the methylated hydrazine fuels MMH, UDMH, and AE-50 led to formation of one or more nitrosoamines at part-per-million levels. Other by-products were also formed, many of them chlorinated. Although it was possible to suppress nitrosoamine concentrations below detectable limits by acidifying the fuel solutions prior to neutralization, no conditions were found in which the formation of other by-products could be eliminated. Although most of these by-products could not be identified, their presence provides sufficient reason to reject the use of hypochlorite for the neutralization of methylated hydrazine fuels under the range of conditions examined in this study.

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